"Development of Porous Composites for Gas Sensing Applications"

A synopsis submitted
to
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SYNOPSIS

Abstract of proposed work plan/ problem

1. Introduction

A composite material is a material made from two or more constituent materials with significantly different physical and chemical properties. Combination of such materials produce a material with character different form the individual components. Especially, composites with porous structure are very important. Such composite materials find number of applications in diverse areas. Moreover, many novel materials with desired structure and property can be tailored using porous materials either as the main matrix or as reinforcing material.

Materials with pores i.e. cavities, channels or interstices are termed as porous materials. Porous materials are categorized into microporous, mesoporous, and macroporous materials as per their pore size. The pore size, arrangement and morphology of the pores, the porosity (the ratio of the total pore volume relative to the apparent volume of the material) and composition of the material itself decide the properties of porous materials. Thus, porous materials belong to a class of materials with low density, large specific surface and a range of unique physical, mechanical, thermal, electrical and acoustical properties. Such materials are used in a wide range of applications like catalysis, chemical separations, adsorbent, ion exchange, energy material, environment material, life sciences, nanotechnology and tissue engineering..

Natural zeolites, synthetic zeolites (from low siliceous zeolites to high siliceous zeolites), pure silica molecular sieves, microporous phosphates, oxides ($AlPO_4$, GeO_2, etc.), and even organic–inorganic hybrid materials such as MOFs can be included in inorganic porous materials category. Zeolite is a family of inorganic, crystalline micro porous materials. Zeolite consists of interconnected aluminosilicate building blocks, which form 3-dimensional frameworks that have void space (cavities or channels) that can hold cations, water, and many other molecules. Their exciting surface and structural properties like high surface area, and therefore their high adsorption capacity and compositional features, as well as ion-exchange properties are being exploited in industrial, agricultural, environmental, and biological applications. Hence, in the

proposed research work, zeolite based porous composites will be developed for detection of various gases.

2. Review of literature and development in the subject (previous work done in the relevant area)

Gas sensors play an important role in many applications and have been extensively developed during the past few decades. This is especially the case for applications in monitoring automotive exhaust gases and air quality.

International status

Xu et al have reported that there are number of possible ways in which the selective properties of zeolite compounds can be utilized for the purpose of gas sensing application [1]. A review on zeolite-based materials in developing approaches to electrochemical and optical sensing is given by Veldes et al [2]. Rauch et al have designed a new sensor by using a Na-A zeolite film to limit the response of the YSZ-platinum amperometric sensor to carbon dioxide while maintaining high sensitivity to oxygen [3]. A new improved CO2 sensor for air quality control was developed by using a combination of a Na3Zr2Si2PO12 _NASICON with the introduction of a zeolite filter was by Kaneyasu and group [4]. Kamonsawas and group found the improvement in sensitivity behaviour towards NH_4NO_3 by introducing zeolite Y into PPV [5]. The review by Sahner et al has revealed that zeolites layers add an auxiliary functionality such as filters or immobilization to the sensors and also have explored the versatility of zeolites in gas sensor field [6]. Vilaseca et al have grown zeolite films on SnO_2 sensors to modify their response and selectivity to gas. They observed that sensor behaviour and the improvement of sensor selectivity increased with the quality of the zeolite layer and the best zeolite films were obtained on SnO_2 layers pretreated at 450 °C [7]. The QCMs coated with Ag+-ZSM-5 zeolite sensors are presented for medical diagnosis by Huang et al [8]. N. Densakulpraserta found that the zeolite content has increased the sensitivity and response time of CO gas for the PANI/zeolite- composite by using the zeolite Y, 13X and A1MCM-41 [9]. Giannakopoulos and group have demonstrated a carbon dioxide sensor using fauzasite-metglass composite [10]. C. Chuapradit et al have investigated effect of LTA type zeolite and zeolite content on electrical conductivity response of zeolite/polyaniline composites when exposed to CO gas under the atmospheric condition [11]. Xu et al studied hydrogen sensing behaviour of nano–tin oxide /NaY zeolite composite. The same group has given a review on use of zeolite and zeolite based materials for developing gas sensors. The

survey explored that the unique properties of zeolites towards a specific gas enhances the sensitivity [12]. Franke and group optimized the variable gas parameters for H-ZSM-5 zeolite with very fast response for least detection limit of ammonia gas [13]. Zeolites MFI and LTA have been used to detect alcohols and alkanes at an operating temperature of 350^0C. The pt-doped SnO_2 gas sensors, covered with zeolite films (MFA and LTA), have been used to detect methane, propane and ethanol by Vilaseca et al. The sensitivity and selectivity were tested for to 1 ppm acetone vapor. They have shown that the zeolite (silicalite and zeolite A) over layer has improved the sensitivity of pt-doped SnO_2 gas sensors for H_2O, H_2, CO, CH_4, C_3H_8, and C_2H_5OH, at concentrations (from 20 to 10,000 ppm) [14]. Thick film sensors were prepared by screen printing layers of chromium titanium oxide (CTO) with various zeolites as over-layers. The sensors gas response was tested against two similar gases; ethanol and isopropyl alcohol. The modified sensors effectively discriminated between the two gases. The zeolite modified and unmodified CTO sensors give response to 80 ppm ethanol at 400^0C [15-16]. Electrical conductivity response and sensitivity of ZSM-5, Y and modernite zeolite to ethanol have been investigated by Intira Y et at and found that H form of these zeolites are more sensitive to ethanol than pure form [17]. Cantilevers, made up of silicon wafer material coated with zeolite (Co-beta) and also with various polymers like PEUT, PECH and PIB, are used for ethanol sensing and it has been observed that zeolite sensing layer gives higher response to ethanol compared to polymers [18]. Zeolite modified micro-cantilever gas sensor has been employed for indoor air quality control [19]. O. Schaf et al have carried out work on single crystal stilbite for alcohol sensing by measuring electrical impedance [20-22]. Pugh et al found that in case of ZnO, modification by zeolite layer leads to increase in sensitivity of sensor compared to unmodified ZnO sensors to low ppm concentrations of acetone, ammonia and ethanol [23]. Pongpol Choeichom et al has carried out detail study on sensing performances of ZSM-5, Y, mordenite, ferrierite, beta, 3A, 4A, 5A, and 13X zeolites towards sulfur dioxide [24].

National Status

The ammonia gas sensing performance of aluminosilicate azide cancrinite zeolite has been reported by Borhade [25]. Joshi et have developed LPG sensor based on vanadium modified zeolite [26]. Khairnar and group have developed a new sensor for ethanol sensing using NaA zeolite [27]. Mahabole and co-workers have developed the novel ethanol sensors using pure natural stilbite zeolite, Mg-exchanged stilbite and ZnO/stilbite composite as main functional

materials [28-30]. The same group also has employed nano-ZSM-5 for ethanol sensing studies [31]. Jamuna et al have developed zeolite based hydro carbon sensor [32]. The possibility of the uses of zeolites and zeolite-based materials for developing gas sensors is tinted and avenues for further research have been suggested by Mohan et al [33] Muzzaffar Ahmad Mir et al has reviewed Zeolite / polymer composites for gas sensing applications[34].

Literature review reveals that zeolites are alternative materials for sensor applications. In most of the cases, zeolites are being employed as a filter layer on certain surfaces for the detection of various gases with improved gas sensing parameters. There are very few reports on sensors wherein zeolite is used as a main functional material. Moreover, very meager work is carried out on zeolite based composites.

3. Objectives of the research

The proposed objectives of the research work are as follows:

1. To develop porous composites for gas sensing application
2. To characterize the synthesized /procured zeolites using various characterization techniques such as XRD, FTIR, TG/DTA, XPS or SEM/ EDAX
3. To prepare zeolite based composites with variable compositions (variable amount of zeolite and various reinforcing materials)
4. To characterize composites by XRD, FTIR, TG/DTA, XPS or SEM/ EDAX
5. To prepare zeolite and zeolite based composite films via suitable method
6. To study the feasibility of zeolite films and zeolite based composite films for gas sensor application
7. To optimize the sensing parameters like operating temperature, response and recovery times, and gas upload capacity etc.
8. To investigate the effect of concentration of reinforcing material and film thickness on the sensing performance

4. Methodology

Composites, with variation in filler content, will be prepared. Composites will be characterized by various techniques for structural and morphological analysis. Thick film will be prepared by using composites as functional material by means of screen printing technique/or by casting method. The substrate for thick film deposition will be either glass or alumina ceramic material. The films deposited on the suitable substrate will be used as sensor films. Homemade two probe

electrical experimental set up will be used for carrying out sensor studies. Operating temperature of a composite sensor will be evaluated for various gas concentrations as well as at various temperatures for fixed gas concentration. Gas response and recovery time will be studied from point view of utilizing these systems for gas sensing devices.

5. Importance of study / society applications

In this work, efforts will be made to develop composite gas sensors that will work at low operating temperature. The developed gas sensors are expected to give quick response to specific gas (toxic gas) with low concentration.

Thus, the developed sensor will help in reducing energy consumption. Detection of toxic gases, with lowest possible concentration, by these sensors in turn will help in reducing air pollution. Thus, the study has societal importance because developed sensors will help in environment protection.

Significance of the study

The study will lead to the development of new kind of gas sensors using entirely different type of zeolite composites. The study, in particular, will be useful in sensing the variety of toxic gases and vapours when they are present in small amounts. Such sensors will be useful in detecting & monitoring environment. The results obtained by carrying out this research work will also be beneficial to various industries especially in chemical and pharmaceutical industries.

6. Proposed work plan/ formulation and structure of study:

It is proposed to make an intensive literature survey in the gas sensors pertaining to zeolites. Porous zeolite will be taken up as a base substrate (sensor bed) will be modified by physical mixing and also by chemical mixing with the help of various fillers. These sensor beds will be investigated for their sensing behavior for various gases/vapors as a function of gas concentrations and also as a function of sensor bed temperature. The sensor material will be characterized by XRD, FTIR, TG/DTA/ and BET for structural determination, thermal behaviour analysis and porosity. The two probe set up will be used for carrying out the resistivity measurement. This will provide the gas sensitivity as a function of temperature. Similar experiments will be carried out for different ppm concentrations of gases/vapours. The response and recovery characteristics will be investigated to see its practical and commercial use as sensor device. The developed sensors will be compared with the existing sensors.

Year-wise plan

The following work will be carried out as per the time duration listed below.

First Year: Completion of pre-Ph.D. guide's course, literature survey, synthesis of samples, understanding of experimental setup, to gain expertise in handling sophisticated instruments like XRD, TGA, UV-VIS and FTIR, development of screen printing set up and to have expertise in screen printing technique, its standardization, participation in seminar/ conference/symposium.

Second Year: Characterization of synthesized samples, standardization of process of composite preparation, effect of variable concentration of filler, characterization by XRD, TGA, AFM, FTIR, etc. for physical and chemical investigations, AFM study of sensor surface, paper publications, participation and presentation in International Conferences.

Third Year: Investigation of gas sensing behavior of bare zeolite and composite thick film sensors for detection of toxic gases such as ammonia, methanol, ethanol, propanol, CO, and CO_2 etc, paper publications, thesis writing and submission.

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